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The funding from this grant was utilized to further develop a new approach for the electronic structure of materials. The method formulates the Kohn-Sham equations of Density Functional Theory directly in real space with a high order Finite Difference approach. The resulting equations were solved using the linear scaling multigrid algorithm developed by Brandt and coworkers. Multigrid techniques were used to solve both the self consistent eigenvalue equations and the Poisson equation for the electrostatic potential at each step of iterations. Accurate numerical results were obtained for finite and periodic electrostatic problems and for the eigenvalue equations for many electron atoms and simple molecules. Recently, conservative grid equations have been developed so that grid refinement strategies can be employed. This allows one to perform extensive numerical work selectively in regions of high electron density. The new method should have wide applications for numerical studies of complex and disordered materials which require a quantum mechanical treatment for many atoms.

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FINAL GRANT REPORT

Multigrid Method for Large Scale Electronic Structure of Materials

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Abstract

The funding from this grant was utilized to further develop a new approach for the electronic structure of materials. The method formulates the Kohn-Sham equations of Density Functional Theory directly in real space with a high order Finite Difference approach. The resulting equations were solved using the linear scaling multigrid algorithm developed by Brandt and coworkers. Multigrid techniques were used to solve both the self consistent eigenvalue equations and the Poisson equation for the electrostatic potential at each step of iterations. Accurate numerical results were obtained for finite and periodic electrostatic problems and for the eigenvalue equations for many electron atoms and simple molecules. Recently, conservative grid equations have been developed so that grid refinement strategies can be employed. This allows one to perform extensive numerical work selectively in regions of high electron density. The new method should have wide applications for numerical studies of complex and disordered materials which require a quantum mechanical treatment for many atoms.

Final Report

Many computations in chemistry require treatments which go beyond effective pair or triplet intermolecular potentials. Examples are chemical reactions in solution, plasma chemistry, glasses with complex covalent networks, high pressure phase diagrams, interactions of molecules with metal surfaces, responses of large systems to electromagnetic fields, *etc.* Quantum mechanical computations on large systems have been limited by the scaling properties of existing algorithms. In recent years extensive effort has gone into developing methods which result in better scaling properties. With the support from AFOSR, we have developed a new approach which utilizes a multigrid (MG) solver[1,2] for both the Kohn-Sham equations and the Poisson equation.[3–8] The method scales in computer time linearly with the number of electrons if the orbitals can be localized in real space (and still yield a realistic description of the ground state electron density). Our calculations so far have been all electron calculations with bare nuclear charges.

In our first study,[4] we developed a multiscale approach for solving the Kohn-Sham equations in real space. A high order (8th) finite difference (FD) representation was used for the

kinetic energy operator in order to obtain numerical accuracy with reasonable sized grids. The nucleus was represented as a discrete charge on the grid with spacial extent that of the finest scale grid size h. The Kohn-Sham equations were solved first on the coarse scale; then the solution was interpolated to the next finer scale and iterations were initiated there. This method does not guarantee a linear scaling solution due to the phenomenon of aliasing of high frequency modes on the coarse scale. However, we obtained accurate numerical results in all electron calculations with uniform grids, and the multiscale method led to substantial accelerations toward the solution. This reflects the presence of critical slowing down (CSD) in the solution process and indicates the importance of multiple length scales in the electronic structure problem. By just iterating on the fine scale alone, it appears one is not even guaranteed of approaching the correct solution in a reasonable amount of time.

In a second paper,[3] we presented our high order MG method for solving the Poisson equation which is required at each self consistency iteration in the Kohn-Sham equations. We tested the method on several finite and periodic problems to determine its efficiency and accuracy. We obtained accurate results for a simple model for atoms with a discrete nuclear charge at the origin and a balancing electron distribution. Accurate results were also obtained for periodic lattice computations in 3-d. This means the method can handle long ranged Coulomb problems without requiring implementation of the Ewald method. By placing the nuclei on the grid as discrete charges, the electrons and nuclei are on an equal footing in terms of solution of the Poisson equation. The linear scaling attributes of the algorithm were demonstrated numerically. The solver was used to generate an accurate electrostatic map of a model zeolite solid. In a subsequent report,[6] similar computations were performed for a 4096 ion solid. The complete solution of the Poisson equation on a 128^3 grid starting from $\phi(\mathbf{r})=0$ everywhere took 3 seconds on the OSC Cray-YMP. We are currently using the high order Poisson solver to carry out Monte Carlo simulations of ionic fluids to test its viability as a general method for electrostatic computations in molecular simulations.

Recently, we have successfully incorporated the nonlinear full approximation scheme (FAS) MG eigenvalue solver of Brandt, *et al.*[9] into our method.[7] This work was presented at the International Paris DFT Meeting of 1995. With this algorithm, we obtained accurate ground state results for the Ne atom (all electrons) with on the order of only 10 fine scale iterations. The full MG solver outperforms the nested procedure, although the nested iteration does yield comparably accurate results. The solution of the Kohn-Sham equations is a nonlinear problem, which requires an MG method going beyond the standard approach typical for linear elliptic problems such as the Poisson equation. We summarized our approach, numerical results, limitations, and future plans in this paper.

In recent months we have begin to examine grid refinement strategies, which are required to obtain accurate numerical results with reasonable grid sizes.[10] We have utlized the techniques of Bai and Brandt[11] for solving the Poisson equation in regions where the potential varies rapidly, namely near the nucleus. Their formulation was developed for 2nd order equations, and we are currently working in collaboration with Achi Brandt on a higher order method. Conservative equations are required because, when the difference equations are set

up for the coarse scale iterations, the 'defect correction' τ leads to a nonconserved source within the finite refinement zone. This can pollute the solution over long ranges for singular sources. We have implemented for the first time the Bai and Brandt technique for three dimensional finite and periodic domains and singular sources, and have obtained promising numerical results with their 2nd order method. The higher order formulation will be crucial in solving real world problems on grids of approachable sizes. These techniques should have applications in several areas of computational physics and chemistry. Our focus will be to use the refinement methods in the region around the atomic nucleus to obtain increased resolution in the core.

In a related project, we have developed a novel approach for computation of chemical potentials and phase equlibria in dense fluids.[12] The method uses the Kirkwood-Buff theory of solutions and an inversion procedure developed by Ben-Naim to compute thermodynamic derivative information. This information is used to extrapolate the chemical potentials around a given state point. The phase diagram of high pressure He/H_2 fluid mixtures was successfully computed. Our intention is to go to even higher pressures (near 1 Megabar) where the hydrogen component can become metallic. The phase diagram of the mixture is unknown there, and has an impact on our understanding of the evolution of the planet Jupiter. The multigrid electronic structure solver will be used in conjunction with the statistical mechanical methods to attempt for the first time to compute a physical phase diagram from *ab initio* quantum mechanics. If the work is successful it will pave the way for simulations of more chemically complex mixtures, such as occur in the interior of Earth.

The funding from this AFOSR grant was used to partially support two fine postdoctoral researchers, Dr. Karthik Iyer and Dr. Anping Liu, for several months while they worked on the FAS eigenvalue problem and related statistical mechanical computations. The research is currently funded by an NSF grant and further support will be sought from AFOSR in the near future. Reprints of our research papers our enclosed.

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